

A Novel Field Portable Plasma Source Monitor for Real Time Air Particulate Monitoring

Yixiang Duan*, Yongxuan Su, Zhe Jin

*Chemical Science and Technology Division, CST-9, MS K484, Los Alamos National
Laboratory, Los Alamos, NM 87545*

Stephen P. Abeln

*Material Science and Technology Division, MST-6, MS G770, Los Alamos National
Laboratory, Los Alamos, NM 87545*

*To whom correspondence should be addressed. Email: yduan@lanl.gov

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In this research, a novel portable instrument for on-site, real-time air particulate monitoring was developed. It is highly desirable to use microwave plasmas for on-site, real-time environmental and occupational hazard monitoring because they can be sustained with various gases at relatively low power and possess excellent detection capabilities for both metal and nonmetal air pollutants. In the new instrument design, a microwave plasma was selected as an excitation source and was used in conjunction with atomic emission spectrometry. A small, integrated spectrometer with a charge-coupled detector (CCD) was used for optical signal detection. An efficient, in-situ air sampling system was developed for direct-sampling air particles into the plasma. Characterization and calibration of the new instrument was achieved with an in-house fabricated high efficiency nebulization-desolvation system. Tolerance of the microwave argon plasma source to air introduction was tested, and the operational parameters were optimized. Analytical performance and the feasibility of the newly developed portable instrument for aerosol particle analysis were evaluated. Some advantages and possible applications of the new instrument are discussed. The instrument provides an innovative tool for rapid environmental and occupational hazard monitoring.

Air pollution is a growing problem and air particulates generated by incomplete combustion of fossil fuels from factories and automobiles are obvious in sky. Federal legislators have been considering airborne particles and various exhaust gaseous streams as serious contributors to global pollution. The Clean Air Act authorizes a nationwide program to reduce air pollution through air quality planning, monitoring, regulation, enforcement, and research. The US Environmental Protection Agency (EPA) set a series of rules and restrictions to minimize potential hazards to both humans and the environment [1]. Based on these regulations and requirements, characterization of air particulates has become even more important than ever for environmental research and occupational safety. These driving forces clearly indicate an urgent need to develop effective methods and technologies for air particulate monitoring and control.

Traditional methods for monitoring airborne particles are both labor-intensive and time-consuming [2-3]. The air particulates are collected via directed flow through a filter with pore size ranging from 0.05 to 5 μm for a number of hours. The filter media is then chemically digested to obtain a mineralized solution and analyzed by an appropriate spectrometry technique such as atomic absorption, atomic emission, and mass spectrometry [4-10]. The entire process of sampling and analysis may take days to get results. For these laboratory-based analysis procedures, appropriate sample handling, preservation, and storage techniques have to be used to prevent sample loss and contamination. Furthermore, these approaches provide only time-averaged airborne concentrations, and are not applicable for transient events because of their integrative nature. Since the analytical results are only available after the fact, they have very

limited value in terms of process control for pollution prevention and occupational safety. Alternatively, immobilized solid particles can be directly analyzed nondestructively by X-ray fluorescence, particle-induced X-ray emission, and neutron activation analysis [11-12]. However, these techniques have other shortcomings, such as low sensitivity for low-Z elements, quantification difficulties and only applicable to immobilized solid particles. More recently, glow discharges have been explored as a tool for air particulate analysis coupling with mass spectrometry and atomic emission spectrometry [13-15]. The sampling air was sucked by a pump through a single-orifice impactor stage, and the aerosols are impacted on a metal support to form a central spot, which was then used as a cathode for glow discharge sputtering and mass spectrometry analysis [14]. A particle beam/momentum separator apparatus was also used for introducing airborne particles into the glow discharge [15].

In recent years, the recognized need for a continuous monitoring in hazardous sites has stimulated research work to adapt laboratory instruments for field tests. Several analytical techniques have been explored with varying levels of success for continuous or real-time monitoring of metals in stationary source emissions and other gaseous particle process streams [16-24]. One of the most widely applied techniques is plasma source atomic emission spectrometry, in which the plasma source provides sufficient energy to atomize and excite metal elements present in working sites and gaseous streams. In these studies, most work has been done to adapt or slightly modify a laboratory inductively coupled plasma (ICP) atomic emission spectrometer (AES) for real-time measurements [16-23]. Because of the low tolerance of ICP plasmas to air samples and the significant differences in both electrical and thermal properties of argon and air, the introduction of

an air sample into an argon ICP plasma is extremely difficult [19-21,25]. During this process, particular attention must be paid to select the proper torch geometry, gas flow rates, and the applied power to achieve the best interaction and energy transfer between the argon plasma and the air-dominated analytical region in the center of the plasma [25]. The stability of an ICP is closely dependent on gas composition and flow rates. Therefore, specially designed sampling interfaces are required to provide a suitable flow for the ICP plasma in order to make effective sampling possible. Meyer and Lee [21] used a virtual impactor sampling interface to introduce and concentrate air samples into the plasma. The drawback of that system is that only heavier particles tend to pass straight through the impactor due to inertia, while the smaller and lighter particles follow the higher gas velocity and flow past the sampling orifice and towards the pump. Obviously, this sampling process results in a significant loss of fine particles, which are the most important components in environmental contamination and hazards. Seltzer et al. [19] designed an automated sampling system consisting of a sampling nozzle, flow sensors, two switches, and a regulated pump with 50-foot heated sample line. With such a device, periodic introduction of aliquots of sample air and reference air at low flow rates was achieved for air particulate monitoring. Water vapor in the sample air was removed through a pair of water-cooled condensers. This sampling interface is much more complicated than the one used in EPA method #29 [2] and has been noted as a potential source for measurement error [19]. In addition, ICP-AES suffers from instrumental complexity, heavy weight, large power consumption, and the absolute need for high flow of supporting gases. These limitations restrict, to some extent, the applications of the technique for on-site, real-time monitoring.

Laser spark based instruments and methods, such as laser induced breakdown spectroscopy (LIBS), have also been explored as an alternative method for air particulate monitoring [26-30]. A high power pulsed laser beam is focused into an effluent, and creates a plasma. The light emitted from the plasma at a certain time delay after the laser spark is spectrally recorded and analyzed. The technique provides a true *in situ* sampling and measurement for direct chemical analysis. Since there is no laborious sample preparation required, the method has much less risk from sample contamination compared to conventional laboratory approaches. However, due to the small focused spot size of the laser beam, the short sampling time, and the low pulse repetition rate, the sample utilization efficiency is quite low for gaseous samples. This small sampling volume results in lower sensitivity for the laser spark technique compared with other methods for gaseous samples. In addition, the stability of LIBS signals is very limited due to the nature of the method. Several factors contribute significantly to fluctuation, such as the laser beam intensity fluctuating, and the emission light depending on the sample matrices and also its physical and chemical characteristics. In the case of aerosol analysis, these fluctuations are even more serious [31]. The detection limits of the method vary from the ppm level (metals) to 50 ppm level (soil) and up to percentage level (gases and airborne aerosols) [31].

The clear demand from environmental monitoring and control, occupational exposure and safety have motivated us to develop a field portable instrument for on-site, real time air particulate monitoring. In this research, a novel portable instrument was designed and assembled with a modified microwave plasma source coupled to atomic emission spectrometry. A small, efficient, integrated spectrometer was used for optical

emission beam dispersal and collection. An inexpensive charge-coupling detector (CCD) was installed for signal detection and processing. A high efficiency, in-situ sampling system was built for direct sampling air particles into the plasma. The instrument was characterized and calibrated with an in-house fabricated nebulization-desolvation system. Influence factors from experimental/operational parameters were examined and optimized throughout the work. Tolerance of the microwave argon plasma source to air was tested. Several elements were selected for the primary examination. Analytical performance and feasibility of the newly developed portable instrument for aerosol particle analysis were evaluated. The system possesses a series of advantages, including high sensitivities for both metal and nonmetal air hazardous; in-situ air sampling without sample collection and pretreatment; compact structure with very limited volume; low power consumption with battery-powered possibility; low construction and maintain costs; and ease of operation in harsh environmental conditions. The portable instrument provides an innovative tool for timely environmental and occupational hazard monitoring, which is very critical for environmental assessment and control, occupational disease prevention, and industrial hygiene inspection.

EXPERIMENTAL SECTION

Instrument design and assembly. The new instrument consists of an excitation plasma source, an optical beam collection and transportation assembly, an integrated optical beam dispersal device, a signal detector, an in-situ air particulate sampling system, and a computer control data processing system. Figure 1 shows the schematic diagram of the instrument assembly. The dimension of the prototype instrument is 19" x

12" x 26". The plasma source is one of the key points in the new instrument design and development. A recently developed microwave plasma generation device [32], called microwave plasma torch, has been demonstrated to be an excellent source for solution sample analysis with atomic emission spectrometry, mass spectrometry, and fluorescence spectrometry [32-39]. The flame-like plasma formed by the microwave discharge shows very good performance with liquid solution sampling and chemically generated vapor sampling [38]. The coaxial configuration of the torch offers some additional advantages over conventional microwave plasma sources [40-43]. However, for this particular instrument design in the current work, we prefer a much smaller size torch to make the instrument portable and compact. For this purpose, a miniature microwave plasma source was developed based on the original design [32]. Some significant modifications have been made to match the needs of the instrument design. The new torch uses one-fourth wavelength in a 2450 MHz power supply instead of the three-fourths wavelength torch used in the literature [32-39]. Various materials were tested for the central tube of the torch, including copper, stainless steel, quartz, and ceramic [44]. It was found that stainless steel and ceramic tubes give the best performance in terms of sample erosion tolerance and plasma stabilization. The torch is set on an X-Y-Z three-dimensional adjustable stage for precise alignment of the optical beam-collection system. An UV-protected window was installed in front panel of the instrument for observing the plasma performance. The torch is connected to a 2450 MHz microwave power supply (Model GMP-03K/SM, SAIREM S.A., France) through a one-meter 50 Ω co-axial cable. Optical beams emitted from the plasma source are collected with optical fibers and lenses in a side-on view mode. A collimating lens was installed at one end of the fiber and placed

toward the plasma to collect emission beam and focus the beam into the fiber optics. A customer-designed, integrated spectrometer with two gratings was used for optical beam dispersal and signal measurement. A Sony ILX511 linear CCD array detector with 2048 element pixels was installed for instantaneous measurements of analyte signals. Wavelengths from about 200 to 450 nm are covered by the spectrometer. A 200-micron diameter fiber and 2400 grooves/mm gratings were most frequently used for the instrument. The software used for data collection has an advanced acquisition and display program that provides a real-time interface to the signal-processing. A notebook computer with a 100 kHz sampling frequency DAQ-700 card (National Instruments INC., USA) is used to show real time spectrum and store data. An interface cable is used to make a connection between the spectrometer and the computer.

Air sampling. Since there is no sample preparation process required for this on-site monitoring, a simple, effective in-situ air-sampling device is necessary for the new portable instrument. Such an air-sampling device was developed with a commercially available air sampling pump (BUCK GENIE, A.P. Buck Inc., Orlando, FL) and a self-assembled gas control system. The small air-sampling pump is designed to collect air samples using industrial hygiene principles and techniques and can be operated at flow rates from 5 to 800 ml/min. The pump, with completely digital control, is used in the new instrument to deliver air particulates into the plasma through the central channel of the torch. In order to minimize influence from moisture difference in real air samples, a sieve sorbent drier was used to absorb the extra water vapor in the air just before the inlet of the central channel of the torch. This sampling design makes the system possible for *in situ* sampling similar to the laser spark technique, but with much larger sampling volumes.

Aerosol generation and system calibration. Since standard metal aerosols or air particulates as calibration gases are hard to find from commercial sources, metal aerosols of known concentration have to be generated in some way for calibration purpose. In this work, a high efficiency nebulization-desolvation system was built to quantitatively convert aqueous solution into dry aerosol for system calibration and the new instrument characterization. Standard solutions with metals of interest can be delivered through a commercial peristaltic pump (Minipuls 3, Gilson Medical electronics INC.) into an ultrasonic nebulizer (U-5000 AT, CETAC Technologies INC.), where the liquid solutions are generated into fine, wet aerosols through an ultrasonic transducer. The ultrasonic nebulizer itself employs a desolvation system to separate and remove most of the moisture in the generated aerosols. The aerosol generation efficiency by the nebulization system is estimated to be 10% with a sample uptake rate of 0.75 ml/min. To further control the solvent loading and simulate “real aerosol” in the air, an additional high efficiency desolvation device was designed and built specifically for this new instrument. This desolvation device includes a two-step desolvation process. A membrane desolvator, with a stainless steel chamber, is used for the first stage. A nitrogen gas stream of about 0.5 L/min flow rate was introduced into the space between the stainless steel chamber and the membrane tube to remove the water vapor produced during the desolvation process. A heating tape was placed at entrance of the membrane tubing to increase the membrane desolvation efficiency. The exit of the membrane desolvator was connected with a sieve sorbent device to further absorb the residue water vapor. With this arrangement, the desolvation efficiency obtained with this new system is comparable to that of the previous system discussed in the literature [45]. However, this new system

seems much easier to handle and operate. This nebulization-desolvation device was found to provide highly reproducible results and was therefore adopted as the basis for air particulate calibration and measurement.

Operational procedure and conditions. A short warm up period for both ultrasonic nebulizer and the microwave power generator is necessary. After proper tune up, the microwave plasma can be generated with an initial forward power of around 30 W, and can be operated from 50 W to 300 W, which is the maximum output for this power supply. Appropriate adjustment of the torch can further minimize the reflected power, which is usually less than 10 W during operation. Plasma gas flow rate can vary in a range from about tens of milliliters to several liters per minute based on the requirements. The sampling pump delivers air at a very low flow rate during the initial step, and is then gradually increased to about 0.2 l/min after a few seconds. Typical operational conditions of the instrument are outlined in Table 1 unless otherwise stated. The resultant spectrum of the air particulate is shown on the screen of the notebook computer, and then stored.

Chemicals and reagents. High purity argon (99.999%, Trigas Industrial Gases, USA) is used as working gas for supporting the plasma. Stock solutions from J.T. Baker INC, USA are used for generating aerosol particles. De-ionized water and analytical purity grade nitric acid are used throughout the work for preparation of working standards and aerosol generation whenever needed.

RESULTS AND DISCUSSION

Features of the instrument design and observations. In order to develop a portable instrument, several factors must be considered in the design process. For example, the plasma source and its power supply system were considered to be one of the most important factors in the instrument design and were intended to be as simple as possible to keep the instrument small and portable. In addition, the plasma source should also be robust enough to withstand direct air sampling and have good tolerance to air particulates. Although ICP plasmas provide efficient energy for air particulate vaporizing and excitation, they suffer from the problems of complex structure, a heavy, relatively large power system, and absolute need of high flow rate supporting gas to maintain the plasmas. Microwave induced plasma (MIP) is also a powerful alternative source for elemental determination that has found extensive use in analytical atomic spectrometry [33]. Compared with other types of plasma sources, the MIP offers some attractive characteristics, such as its unique features of high excitation efficiency for both metal and nonmetal elements, the capability of working with various gases, low complexity, low power consumption, and low cost. In addition, better air tolerance from microwave plasmas than that of the ICPs makes them a stronger competitor for the plasma source selection for our portable instrument. As microwave plasmas can be sustained at low power and low gas flow rate and can be operated in a continuous operation mode, it is desirable to use microwave plasma for on-site, real time air pollutant monitoring.

The flame-like plasma formed by our small torch is a toroidal when argon is used as both plasma and carrier gases. As shown in Figure 2 (a), the plasma formed on the top of the torch between the intermediate tube and the central tube extends outwards several

centimeters into air. The lower portion of the pure argon plasma takes a small cone shape, and the higher portion of the plasma takes a candle-flame shape. When air is introduced into the central channel, the plasma shape changed from two obvious portions into one candle-like plasma, which is shown in Figure 2 (b). An obvious central channel caused by the air flow can be observed with more brilliant white color. From the comparison between Figure 2 (a) and (b) that were obtained under the same operational conditions, we also can see significant plasma volume change due to air introduction. However, this volume change does not have an observable influence on optical beam collection when the self-developed focusing lens system is used.

Plasma tolerance to air. Plasma tolerance to air introduction is one of the key issues in the success of the project. In order to test the feasibility of the new instrument for direct air particulate monitoring, several approaches have been explored to introduce air samples into the plasma. At the initial step, argon plasma gas was used to sustain plasma through the intermediate tube, and air samples are introduced through the central channel. Although this is a functional way to introduce air samples, low plasma tolerance was found and less interaction and energy transfer between the argon plasma and air-dominated central channel was identified. To enhance the interaction and energy transfer between the analytes and the argon excitation species, an additional central channel with a much smaller diameter was tested to introduce another portion of argon gas into the plasma. In this way, an argon-air-argon sandwich-type sampling was formed, which can significantly increase the plasma tolerance to air. Finally, we found that a well pre-mixed argon-air gas for sampling through the central channel can also enhance the plasma tolerance. With this arrangement, a typical argon tolerance to air of up to 20% can be

achieved. For helium working gas, a preliminary examination showed that up to 40% air could be introduced into the helium plasma without extinguishing the microwave plasma source. It should be noted that the maximum allowable amount of introduced air depends on the argon gas flow rates in the intermediate and central channels.

Optimization of the experimental parameters. For plasma supporting gas flow rate, we found that low flow rates are good for signal intensity due to the high analyte density inside the plasma. However, lower plasma supporting gas flow rate results in a lower tolerance of the plasma to air. After a series of examinations and evaluations, compromised flow rates were set for argon flows at 1.5 L/min. With these flow rates, 0.2 to 0.4 L/min air can be delivered into the plasma without degradation of the plasma performance. Microwave power was found to have the same influence on signal intensity as indicated in our previous work [46]. Usually, higher microwave power leads to a better signal. However, high power creates some potential problems for the portable instrument. With portability and flexibility in mind, a microwave power less than 200 W was usually used in this instrument.

Observation height is another important parameter. Since different elements have different excitation energy, a series of elements were tested for observation height influence. Figure 3 shows the results, which indicate that most elements (Cu, Mn, Mg, Ag, Hg, Zn, Cd) have similar trends from observation height influence and have maximum signal intensity at an observation height of 10 mm above the top of the torch. The only exceptions are Ba and Cr, which have a little bit higher optimum observation height. These results suggest that a compromise observation height of 10 mm may be used for simultaneous multi-elements monitoring.

Atomic and ionic lines. An interesting phenomenon was observed when beryllium air samples were introduced into the plasma. As indicated in our previous publication [46], beryllium is important in occupational safety and must be carefully controlled. A through research has been conducted on beryllium air particulates with this new portable instrument. In our observations, beryllium atomic and ionic lines have quite different responses to air particulate introduction. Overall, the introduced air has a larger influence on the signal intensities of ionic lines than it has on atomic lines. Figure 4 shows air flow rate influence on Be (I) 234.86 nm and Be (II) 313.04/313.10 nm spectral lines. With an increase in the air flow rate, the intensity of the atomic line (234.86 nm) goes up from sharp jumps to a smooth line at all tested flow rate ranges. However, the ionic lines (313.04/313.10 nm) go up with an air flow rate of between 0.15 to 0.2 L/min, and then go down quickly. These results suggest that high air flow rates do not benefit the ionic signals for beryllium measurement. This phenomenon is believed due to the partial loss of plasma energy when air is introduced. As discussed in the references [18], an introduction of air into the plasma will result in a “cooling effect” in the central channel of the plasma, mainly as a result of the dissociation of molecules (main components of air) and the chemical reactions between the plasma components. All of these processes lead to a less energetic plasma when air is introduced. Since ionic lines have much higher energy levels than atomic lines [47] and need more energy for excitation, the air “cooling effect” in the central channel should, as we expected, have a stronger effect on ionic lines than on atomic lines. From this point of view, increasing microwave power should benefit ionic lines. Such an expectation was proved true in our subsequent experiments. Figure 5 shows the power influence on the different spectral

lines for beryllium. It is very clear that increasing microwave power can significantly increase ionic signals. As is seen from Figure 5, at a lower power range, the atomic signals are slightly stronger than ionic signals, and at a higher power range, the ionic signals are much stronger than atomic signals. These results again demonstrate that more energy is required for excitation of ionic spectral lines.

Observation height is another factor that influences both atomic and ionic lines. Figure 6 shows the observation height influence. A maximum intensity for beryllium ionic lines was obtained at an observation height of 9 mm above the torch, and a similar maximum did not come out until the observation height reached 14 mm for the atomic line. These results mean that the lower portion of the plasma is more energetic. However, since all particulates experience evaporation, atomization, and excitation processes when they pass through the plasma, the maximum intensity signal appears at the medium height of the plasma, from 9 to 14 mm, depending on the species. A comparison of atomic and ionic lines has not been done in details for every element at this time. However, we found that manganese atomic and ionic lines had similar behavior to beryllium during our subsequent tests.

Aerosol conversion to air equivalent. Based on the calibration system discussed in the instrumentation section, aerosol concentrations generated from the ultrasonic nebulizer need to be converted into the equivalent amounts of air samples. In this conversion process, several factors are considered, starting from sample uptake rate of the solution standards to final dilution inside of the plasma. For a given element, if an aqueous standard solution concentration is C_s , sample uptake rate from a peristaltic pump

is V_u , and the nebulization efficiency from the nebulizer is E , the concentration of the element in the plasma should be:

$$C_p = C_s \times V_u \times E / F_t \quad (1)$$

Where the C_p is the concentration of the element in the plasma, and the F_t is the total flow rate of all gases. In consideration of the dilution effect of air particulates in the total gas flow rate, a dilution factor D_f should be added to the equation (1). Therefore, the actual air particulate concentration C_{air} should be:

$$C_{air} = C_p \times D_f \quad (2)$$

Where $D_f = F_t/F_a$, and F_a is the air flow rate pumped into the plasma. Combining equations (1) and (2), we obtain:

$$C_{air} = C_s \times V_u \times E/F_a \quad (3)$$

By using equation (3), we can quantitatively convert the standard solution concentration used for the system calibration into an air aerosol equivalent. It should be noted that equation (3) is only effective when the aerosol transport efficiency from the exit of the nebulizer to the top of the plasma torch is assumed to 100%. Actually, the efficiency value of the aerosol transportation is always less than 1 due to the deposit of fine droplets between the nebulizer and the plasma torch. However, in most cases, this deposition

influence is small and can be ignored [45]. As a result, the concentration of pollutant measured in ambient air is conservative, which is favorable in terms of safety.

Analytical performance. Many elements have been tested with this portable instrument. A typical spectrum with multiple elements at solution concentration of 1 $\mu\text{g/ml}$ was obtained at an air flow rate of 0.2 L/min, and is shown in Figure 7. Detection limits of these elements were calculated based on the signal intensities and the standard deviations. The detection limits are defined as the signal being equal to three times the standard deviation. The standard deviations were determined by measuring and calculating the statistical fluctuations on signal intensities for each individual element. All the detection limits were obtained by taking the air flow into account and using the nebulization efficiency as stated above. The equivalent concentrations in air were converted through calculation with equation 3 and are summarized in Table 2. For reference purposes, the detection limits obtained from solution samples with pure argon carrier gas are also listed in Table 2 [44]. Introduction of air reduces the sensitivities for many elements at a range from 5 (Cu) to 75 (Hg) times approximately.

CONCLUSION

A novel field portable plasma source monitor has been successfully developed for continuous, on-site, real time air particulate monitoring. Calibration of the instrument was achieved through a laboratory-built, high-efficiency, nebulization-desolvation device. An efficient, in-situ air sampling system has been developed for direct sampling air particles into the plasma. The instrument can be easily applied to on-site, real-time environmental hazards and occupational exposure monitoring. Tolerance and feasibility tests to air

introduction demonstrate that the microwave plasma source has some advantages over other kinds of plasma sources, such as ICP. The detection limits obtained with the new instrument are favorable for most of the tested elements. The advantages of the new instrument include (1) direct, *in situ* sampling from air without pre-treatment; (2) real time, on-site, continuous monitoring; (3) high sensitivity with good sampling volume; (4) simultaneous multi-channel detection; (5) portability and compact structure; (6) low instrument and operating costs; (7) the possibility of continuous operation without intervention; (8) versatile, multi-function instrument for environmental and occupational monitoring.

This portable, on-site, real-time monitoring instrument could make great contributions to the control of environmental hazards and monitoring of occupational hazard exposure. This new tool will provide regulatory compliance for personal protection and timely information regarding worker safety and hazard exposure. This effective exposure control technique will possibly save lives and money, relieve a tremendous burden upon health care resources and an enormous drain on national productivity. This technique will have significant impact on the current environmental and occupational monitoring technologies.

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Table 1 Operational conditions of the new instrument.**Plasma**

Microwave power	200 W
Plasma supporting gas flow rate	1.5 L/min
Plasma central gas flow rate	1.5 L/min

Sampling and calibration

Air sampling rate	0.2 L/min
Sample up-take Rate	0.75 ml/min
Heating temperature of the ultrasonic nebulizer chamber	140 °C
Cooling temperature of the ultrasonic nebulizer desolvator	-5 °C
Heating temperature of the membrane drier device	80 °C
N ₂ gas flow rate for taking away water vapor	0.5 L/min

Optical and spectrometer set-up

Diameter of fiber optics	200 µm x 2 m
Spectrometer slit	10 µm
Spectrometer grating	2400 grooves/mm
Spectral range	200-450 nm
Pixel resolution	3.2 pixels
Optical resolution	0.25 nm

Data acquisition

Integration time	100 ms
Number of spectrum averages	100

Table 2. Detection limits obtained with the new instrument.

Element	Wavelength (nm)	Detection limits	
		($\mu\text{g}/\text{m}^3$) [*]	(ng/ml) ^{**}
Ag (I)	328.1	0.47	0.21
Ba (I)	455.5	0.37	0.24
Be (II)	313.1	0.21	0.009
(I)	234.9	0.12	0.047
Cd (I)	228.8	1.3	0.41
Cr (I)	425.4	0.31	0.22
Cu (I)	324.7	0.088	0.13
Hg (I)	253.7	4.3	0.44
Mg (I)	285.2	0.14	0.078
Mn (II)	257.6	2.3	0.77
(I)	279.5/279.8	1.3	0.76
Zn (I)	213.8	2.2	0.39

^{*} This work in air equivalent concentrations, calculated with equation (3) for aerosol conversion.

^{**} Cited from reference, values obtained with argon carrier gas only [44].

Figure captions:

Figure 1. Schematic diagram of the portable instrument;

Figure 2. Plasma features with and without air introduction. (a) Without air introduced; (b) With 0.2 L/min air introduced.

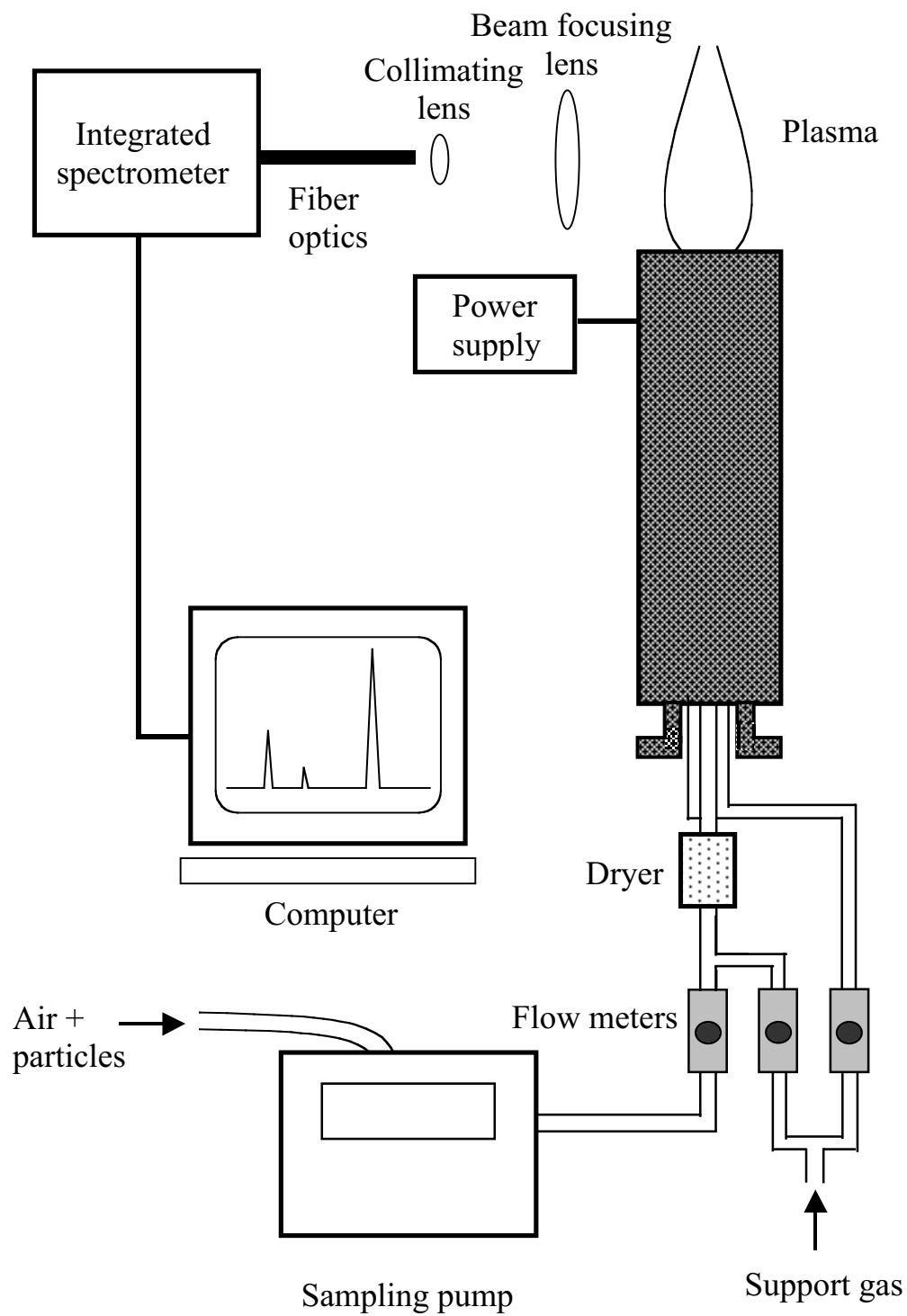
Figure 3. Plasma observation height influence on multiple elements. Concentrations used are 1 $\mu\text{g/ml}$ in solution. Other experimental conditions are as shown in Table 1. \blacklozenge : Cu, \wp : Mn, \blacktriangle : Mg, Δ : Ag, \diamond : Hg, ρ : Zn, \ast : Cd, o: Ba, and Φ : Cr.

Figure 4. Sampling air flow rate influence on beryllium atomic and ionic lines. Experimental conditions used are the same as in Table 1. Beryllium concentration is 0.5 $\mu\text{g/ml}$. \blacktriangle : Be (I) 234.9 nm, and \wp : Be (II) 313.0/313.1 nm.

Figure 5. Microwave power influence on beryllium atomic and ionic signals. Experimental conditions are the same as in Figure 4. \blacktriangle : Be (I) 234.9 nm, and \wp : Be (II) 313.0/313.1 nm.

Figure 6. Observation height influence on beryllium atomic and ionic signals. Experimental conditions are the same as in Figure 4. \blacktriangle : Be (I) 234.9 nm, and \wp : Be (II) 313.0/313.1 nm.

Figure 7. A typical multi-elements spectrum obtained with 1 $\mu\text{g/ml}$ solution of each element at an observation height of 10 mm. Other experimental conditions are the same as in Table 1.





(a)



(b)

